

Nature of the Organic Signature in Dust from the Interstellar Medium: Laboratory Analog Studies

M.M. Freund

NASA Goddard Space Flight Center, Greenbelt, MD

F.T. Freund

Department of Physics, San Jose State University & NASA Ames Research Center

A. Staple and J. Scoville

Stanford University

Abstract

We measured the infrared (IR) ν_{CH} absorption bands around $3.4\mu\text{m}$ ($2800 - 3000\text{cm}^{-1}$) in large laboratory-grown magnesium oxide (MgO) and natural olivine single crystals that crystallized from CO/CO₂/H₂O saturated melts. These bands are very similar to those from many astronomical sources, such as from dust in the diffuse interstellar medium (ISM), from the outflow of evolved stars, etc., and they are characteristic of aliphatic $-\text{CH}_2-$ and $-\text{CH}_3$ entities. In our laboratory single crystals the ν_{CH} bands arise from C-H entities that were introduced by a solid solution process, and that are imbedded in the mineral matrix in form of polyatomic C_n entities with C atoms bonded to O and to H. Heating breaks the C-H bonds, causing hydrogen to disperse in the mineral matrix. C-H bonds are re-established rapidly during annealing. We propose that dust grains probably contain the same type of internal C_n-H entities in solid matrix rather than an external organic layer covering the grain surfaces. Thermodynamical arguments show that the concentration of organics in solid solution in small grains can be comparable to that found in astronomical environments.

1. Introduction

Many dust models have been proposed to account for the optical extinction (O'Donnell *et al.* 1997), and the C - H stretching bands (ν_{CH}) at $3.4\mu\text{m}$ seen in absorption in the IR spectra of diffuse sources in the ISM [for a recent review (Pendleton and Allamandola 2002)]. Most models contain either (a) small carbonaceous grains accounting for the "organic" signature, or (b) silicate grains covered by an ice mantle, photolytically processed to a residue of complex organics, or covered by a veneer of hydrogenated amorphous carbon (HAC). Generally, when solids grow from a gas-saturated melt, or grains condense in gas-rich environments, these gaseous components dissolve in the solid matrix. A relevant example is the dissolution of H₂O and CO₂ in MgO, which includes a solid-state redox conversion of the solutes to chemically reduced C and H (Freund *et al.* 2001). Therefore, laboratory-grown MgO and natural olivine crystals display an "organic" IR signature at $3.4\mu\text{m}$, similar to that seen in diffuse ISM sources (Pendleton *et al.* 1994). In MgO and olivine the carriers of the organic signature consist of C_n-H-O entities inside the matrix. For single crystals, the total C-H concentration is low ($< 100\text{ppm}$), and the $3.4\mu\text{m}$ absorption bands are fairly narrow, as opposed to the broad astronomical absorption bands. However, using thermodynamical arguments, we show that the amount of dissolved "organics" is a strong function of grain size. This allows us to estimate the total C-H contents in small refractory grains, consistent with astronomical observations of the ν_{SiO}/ν_{CH} band ratios.

2. Results

For H₂O in MgO, we write a proton transfer reaction $\text{H}_2\text{O} + \text{O}^{2-} = 2\text{OH}^-$, where two H⁺ substitute for one Mg²⁺. Local charge balance is achieved when two OH⁻ sit next to the Mg²⁺ vacancy. This local configuration is not stable (King and Freund 1984). It converts by way of an electron transfer from O²⁻ to H⁺ to $\text{OH}^- + \text{OH}^- = \text{O}_2^{2-} + \text{H}_2$. Similarly, CO₂ is taken up in solid solution, not necessarily as carbonate ($\text{CO}_2 + \text{O}^{2-} = \text{CO}_3^{2-}$), with concomitant electron transfer from O²⁻ onto C: $\text{CO}_2 + 2\text{O}^{2-} = \text{CO}_2^{2-} + \text{O}_2^{2-}$. Carbon is reduced to formate with C sitting off-center in the Mg²⁺ vacancy. The formate anion further dissociates: $\text{CO}_2^{2-} = \text{CO}^- + \text{O}^-$, with C entering interstitial sites. C and H₂ are subject to segregation into elastically relaxed portions of the mineral structure. When C-H and C-C bonds form at the expense of C-O bonds, polyatomic C_n-H-O entities, so-called "protomolecules", precipitate inside the matrix (Freund *et al.* 2001).

Fig. 1 shows ν_{CH} of a laboratory-grown, high purity MgO crystal and of a gem-quality olivine crystal from the upper mantle. The antisymmetric and symmetric ν_{CH} bands are associated with -CH₂- and -CH₃ entities, respectively, typical of aliphatic organics with C-C single bonds. The -CH₂- to -CH₃ line intensity ratio (taking the background corrected line depth) is quite large: $\sim 8 : 1$ in MgO and $10 : 1$ to $12 : 1$ in olivine. For MgO we also observed a weak ν_{CH} band near 3008cm^{-1} ($3.3\mu\text{m}$), associated with an aromatic CH entity. The strong ν_{CH} bands in MgO are shifted by 4cm^{-1} to higher frequencies compared to those in olivine, and are slightly broader. After crushing the crystals, C_n-H-O entities can be solvent-extracted and thereby converted to organic molecules. Crushed MgO yielded predominantly short-chain carboxylic and dicarboxylic acids (Freund *et al.* 1999). Crushed olivine yielded longer chain-length fatty acids with $6 \leq n \leq 12$ (Gupta and Freund 1998), consistent with the different -CH₂- / -CH₃ line intensity ratios. Upon heating to $550 - 1000\text{K}$, the C-H bonds pyrolyze and the ν_{CH} bands disappear. Upon annealing at $300 - 450\text{K}$, they reappear within a few days to weeks, their intensities increasing linearly with \sqrt{t} , suggesting that the C-H bonds re-establish themselves rapidly during annealing (Freund *et al.* 2001).

Fig. 2 shows the $3.4\mu\text{m}$ band of the Galactic Center source IRS6E (Pendleton *et al.* 1994). The band positions are identical, but are significantly broader, and their relative intensities different from those of the MgO and olivine crystals. The CH₂/CH₃ ratio of 2 - 3 lies in the range of CH₂/CH₃ ratios reported for many sources throughout the galaxy (Sandford *et al.* 1995), suggesting that the ν_{CH} contributions in the organic matter associated with the dust arises mostly from short-chain aliphatic entities, with $n \approx 4 - 6$.

The observed C_n-H-O concentrations in our MgO and olivine crystals are much lower ($< 100\text{ppm}$) than those inferred from astronomical observations ($\sim 10\%$). However, for very small grains very high C_n-H-O concentrations are possible, as can be shown by thermodynamical arguments. The total solute concentration in a grain becomes a function of not only T, but also of grain size

$$C_{total} \approx \kappa_{eq} \exp\left[-\frac{H_{sol}}{KT}\right] + \frac{2r}{d} \frac{\kappa_{eq} \exp\left[\frac{(H_e - H_{sol})}{kT}\right]}{1 + \kappa_{eq} \exp\left[\frac{(H_e - H_{sol})}{kT}\right]},$$

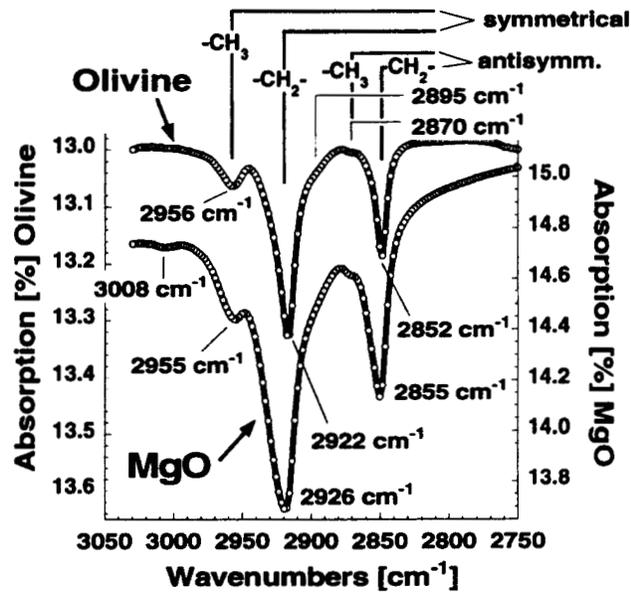


Fig. 1.— The ν_{CH} absorption bands near $3.4\mu\text{m}$ for olivine (upper), and MgO (lower) (see text).

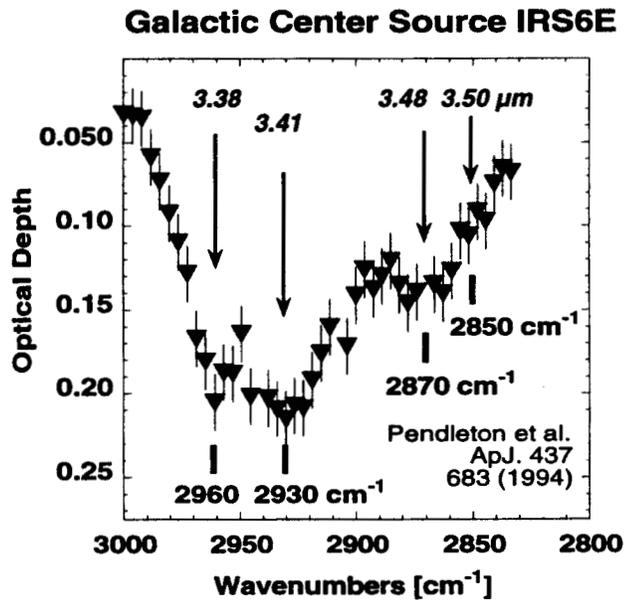


Fig. 2.— The absorption spectra towards the Galactic Center source IRS6E from Pendleton *et al.* (1994).

where H_{sol} is the heat of solution, κ_{eq} is the equilibrium solubility constant, k is the Boltzmann constant, and T is the absolute temperature. The first term is due to the bulk solubility of a solute (C) in a matrix such as MgO. The solubility decreases with decreasing T . In the stiff mineral matrix solute atoms or ions create local stresses, raising the overall energy. The system must respond by lowering the solute concentration. If, however, the solutes can be accommodated where stresses are elastically relaxed, i.e., soft (Freund *et al.* 2001), higher solute concentrations can be maintained. H_e is the strain energy difference between the stiff interior and the elastically relaxed, soft surface region. If d is the surface area per unit volume, the number of occupied soft sites at saturation is $10/dr^2$, where $r = 0.25\text{nm}$ is the width of one atomic layer. Assuming a 5 nm wide "soft" region, with $\kappa_{eq} = 0.06$, $H_e = 80\text{KJ/mole}$ and $H_{sol} = 40\text{KJ/mole}$, we get a solute concentration in the bulk of 2% at $T_{crist} \approx 3000\text{K}$ for MgO, but decreases to $\sim 0.01\text{ppm}$ at 300K . The smaller the grains, the larger C_{total} , reaching 0.5%, 5% and 17% in grains of 100 nm, 10 nm, and 3 nm diameter, respectively.

3. Discussion and Summary

If dust in the ISM consists of a solid solution between the mineral component and $\text{H}_2\text{O}/\text{CO}_2$, formed during condensation from the gas phase, dust grains are expected to contain $\text{C}_n - \text{H} - \text{O}$ entities of aliphatic character in solid matrix. Being imbedded rather than being on the outside, these $\text{C}_n - \text{H} - \text{O}$ are protected from selective sputtering and degradation. The optical depth of the $3.4\mu\text{m}$ feature of dust seems to be well correlated with the $9.7\mu\text{m}$ Si-O stretching band (Sandford *et al.* 1995)), and $\nu_{CH}/\nu_{SiO} \approx 0.1$ is near-constant along most lines of sight that have been studied. Because small grains in our model have high concentrations of organics, a reasonable size distribution has an almost constant CH concentration, without complicated fine tuning of the size distribution. Thus, these "organics" will continue to contribute to the $3.4\mu\text{m}$ band. Likewise, short heat pulses are expected to lead to pyrolysis of the C-H bonds, but the ν_{CH} bands of embedded $\text{C}_n - \text{H} - \text{O}$ entities are likely to recover, as they did in laboratory observations of MgO and olivine crystals.

REFERENCES

- Freund, F., Gupta, A., and Kumar, D., 1999, *Origins Life Evol. Biosphere*, **29**, 489-509.
 Freund, F., Staple, A., and Scoville, J., 2001, *Proc. Natl. Acad. Sci.*, **98**, 2142-2147.
 Gupta, A. and Freund, F., 1998, *Lunar and Planetary Institute Conference 29*, Abstr. No. 1107.
 King, B.V. and Freund, F., 1984, *Phys. Rev. B*, **29**, 5814-5824.
 O'Donnell, J.E. and Mathis, J.S., 1997, *ApJ*, **479**, 806.
 Pendleton, Y.J. and Allamandola, L.J., 2002, *ApJS*, **138**, 75-98.
 Pendleton, Y.J., {*et al.*, 1994, *ApJ*, **437**, 683-696.
 Sandford, S.A., Pendleton, Y.J., and Allamandola, L.J., 1995, *ApJ*, **440**, 697-705.